



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|---|-----------|--|
| (51) International Patent Classification ⁵ : C07C 17/00, 17/20, 17/10 C07C 19/08 | A1 | (11) International Publication Number: WO 94/11327 (43) International Publication Date: 26 May 1994 (26.05.94) |
| (21) International Application Number: PCT/US93/10139 (22) International Filing Date: 29 October 1993 (29.10.93) (30) Priority data: 07/972,663 6 November 1992 (06.11.92) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors: NAPPA, Mario, Joseph ; 3 Oakridge Court, Newark, DE 19711-3435 (US). RAO, Velliyur, Nott, Mallikarjuna ; 1 Georgetown Avenue, Wilmington, DE 19809 (US). (74) Agents: HEISER, David, E. et al.; E.I. Du Pont De Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US). | | (81) Designated States: JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> |
| (54) Title: CATALYTIC CHLOROFLUORINATION PROCESS FOR PRODUCING CHClFCF ₃ AND CHF ₂ CF ₃ (57) Abstract <p>A chlorofluorination process is disclosed which employs a catalyst comprising chromium oxide for producing halohydrocarbons of the formula CHXFCF₃ (where X is selected from Cl and F). The process is characterized by feeding a combination of components comprising (i) at least one halohydrocarbon starting compound selected from CHCl = CCl₂ and CH₂ClCF₃, (ii) hydrogen fluoride and (iii) chlorine, to a reaction zone; contacting said combination of compounds in said reaction zone with a catalyst comprising chromium oxide at an elevated temperature to produce reaction zone products containing halohydrocarbons of the formula CHXFCF₃ together with halohydrocarbon reaction products of the formula CHYClCF₃ (wherein Y is selected from Cl and H); and recovering at least a portion of the reaction zone products from the reaction zone including at least one halohydrocarbon of the formula CHXFCF₃. Optionally, a portion of the reaction zone products can be recycled to the reaction zone; and the combination of components contacted with the catalyst can optionally further comprise at least one halohydrocarbon recycle compound of said formula CHYClCF₃. The process may be controlled to produce halohydrocarbon compounds of the formula CHXFCF₃ in the recovered reaction products as the major components of the halogen-substituted hydrocarbon reaction products in the recovered reaction products.</p> | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | |
|----|--------------------------|----|---------------------------------------|----|--------------------------|
| AT | Austria | GB | United Kingdom | MR | Mauritania |
| AU | Australia | GE | Georgia | MW | Malawi |
| BB | Barbados | GN | Guinea | NE | Niger |
| BE | Belgium | GR | Greece | NL | Netherlands |
| BF | Burkina Faso | HU | Hungary | NO | Norway |
| BG | Bulgaria | IE | Ireland | NZ | New Zealand |
| BJ | Benin | IT | Italy | PL | Poland |
| BR | Brazil | JP | Japan | PT | Portugal |
| BY | Belarus | KE | Kenya | RO | Romania |
| CA | Canada | KG | Kyrgyzstan | RU | Russian Federation |
| CF | Central African Republic | KP | Democratic People's Republic of Korea | SD | Sudan |
| CG | Congo | KR | Republic of Korea | SE | Sweden |
| CH | Switzerland | KZ | Kazakhstan | SI | Slovenia |
| CI | Côte d'Ivoire | LJ | Liechtenstein | SK | Slovakia |
| CM | Cameroon | LK | Sri Lanka | SN | Senegal |
| CN | China | LU | Luxembourg | TD | Chad |
| CS | Czechoslovakia | LV | Latvia | TC | Togo |
| CZ | Czech Republic | MC | Monaco | TJ | Tajikistan |
| DE | Germany | MD | Republic of Moldova | TT | Trinidad and Tobago |
| DK | Denmark | MG | Madagascar | UA | Ukraine |
| ES | Spain | ML | Mali | US | United States of America |
| FI | Finland | MN | Mongolia | UZ | Uzbekistan |
| FR | France | | | VN | Viet Nam |
| GA | Gabon | | | | |

TITLE

CATALYTIC CHLOROFLUORINATION PROCESS FOR
PRODUCING CHClFCF_3 and CHF_2CF_3

5

FIELD OF THE INVENTION

This invention relates to the catalytic
chlorofluorination of halogenated ethanes and ethylenes
containing chlorine, and more particularly to the
production of halogenated ethanes containing fluorine by
10 such chlorofluorination.

BACKGROUND OF THE INVENTION

Many processes have been disclosed for the
preparation of 2-chloro-1,1,1,2-tetrafluoroethane (i.e.,
HCFC-124 or CHClFCF_3) and pentafluoroethane (i.e.,
15 HFC-125 or CHF_2CF_3). Typical processes are described in
GB 1,578,933 and U.S. Patent No. 3,755,477.
GB 1,578,933 suggests hydrodehalogenation of various
halogenated ethanes including 2,2-dichloro-1,1,1,2-
tetrafluoroethane (i.e., CFC-114a or CCl_2FCF_3) and
20 pentafluoroethane, to form 1,1,1,2-tetrafluoroethane
(i.e., HFC-134a or CH_2FCF_3) and HCFC-124. U.S. Patent
No. 3,755,477 discloses a process for producing
fluorinated aliphatic hydrocarbons which comprises
fluorinating a halogenated aliphatic hydrocarbon (e.g.,
25 1,1,1-trichloroethane or trichloroethylene) using a gas
phase reaction with hydrogen fluoride in the presence of
a chromium oxide catalyst. Example 23 therein
illustrates using tetrachloroethylene as a raw material,
with formation of 20% 2,2-dichloro-1,1,1-trifluoroethane
30 (i.e., CHCl_2CF_3 or HCFC-123), 20% HCFC-124, 30% HFC-125
and 20% chloropentafluoroethane (i.e., CClF_2CF_3 or
CFC-115).

It is difficult to predict the supply/demand
situation for any given hydrofluorocarbon, hydrochloro-
35 fluorocarbon or their precursors. There is thus an

SUBSTITUTE SHEET

incentive for developing numerous routes to commercially valuable hydrofluorocarbons and hydrochlorofluorocarbons. HFC-125 and HCFC-124 are useful as refrigerants, blowing agents, fire extinguishants and propellants. Therefore, there is continuing interest in developing efficient methods of producing these materials.

SUMMARY OF THE INVENTION

The present invention provides a process which employs a catalyst comprising chromium oxide for producing halohydrocarbons of the formula CHXFCF_3 (where X is selected from Cl and F). The process is characterized by feeding a combination of components comprising (i) at least one halohydrocarbon starting compound selected from $\text{CHCl}=\text{CCl}_2$ and CH_2ClCF_3 , (ii) hydrogen fluoride and (iii) chlorine, to a reaction zone; contacting said combination of compounds in said reaction zone with a catalyst comprising chromium oxide at an elevated temperature to produce reaction zone products containing halohydrocarbon reaction products of the formula CHXFCF_3 together with halohydrocarbons of the formula CHYClCF_3 (wherein Y is selected from Cl and H); and recovering at least a portion of the reaction products from the reaction zone including at least one halohydrocarbon of the formula CHXFCF_3 . Optionally, a portion of the reaction zone products can be recycled to the reaction zone; and the combination of components contacted with the catalyst can optionally further comprise at least one halohydrocarbon recycle compound of the formula CHYClCF_3 . Advantageous embodiments of the process include providing a contact time and temperature in the reaction zone and an amount of recycle of halohydrocarbons of the formula CHYClCF_3 to the reaction zone sufficient to produce halohydrocarbon compounds of the formula CHXFCF_3 in the recovered

SUBSTITUTE SHEET

reaction products as the major component of the halogen-substituted hydrocarbon reaction products in the recovered reaction products.

DETAILS OF THE INVENTION

5 The present invention provides a process for catalytically chlorofluorinating CH_2ClCF_3 and/or $\text{CHCl}=\text{CCl}_2$ to produce CF_3CHClF and/or CF_3CHF_2 .

10 In accordance with this invention, CH_2ClCF_3 and/or $\text{CHCl}=\text{CCl}_2$, and hydrogen fluoride and chlorine are contacted with a catalyst comprising chromium oxide at elevated temperature to produce CHClFCF_3 and CHF_2CF_3 . Preferably, the catalyst consists essentially of chromium oxide. Most preferably the catalyst consists essentially of chromium oxide prepared as described in
15 U.S. Patent No. 5,036,036, which is hereby incorporated by reference herein in its entirety. This includes catalyst compositions comprising Cr_2O_3 prepared by pyrolysis of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and having an alkali metal content of about 100 ppm or less.

20 The catalysts of this invention facilitate obtaining high yields of the desired products. Preferably, the compounds CH_2ClCF_3 and $\text{CHCl}=\text{CCl}_2$ are converted to provide 2-chloro-1,1,1,2-tetrafluoroethane, pentafluoroethane or in some embodiments, a combination
25 of 2-chloro-1,1,1,2-tetrafluoroethane and pentafluoroethane in total, as the major (i.e., about 50 mole percent or more) chlorofluorination product. Most preferably, the chlorofluorination is run without isomerization of CF_3CHClF or disproportionation of
30 CF_3CHClF or CF_3CHF_2 .

 The chlorofluorination reaction may be conducted in the reaction zone of any suitable reactor, such as a fixed bed reactor. It may be done in a batch or continuous mode; and may be conducted in a single
35 reaction vessel or a combination of reaction vessels.

SUBSTITUTE SHEET

The reaction vessel(s) of the reactor should be constructed of materials which are resistant to the corrosive effects of hydrogen fluoride, hydrogen chloride, and chlorine, such as Hastelloy™ nickel alloy and Inconel™ nickel alloy.

The reaction may be run with or without recycle of at least one halohydrocarbon of the formula CH_2ClCF_3 from the reaction products. Where no recycle is practiced the halohydrocarbon(s) fed to the reaction zone typically consist essentially of CH_2ClCF_3 and/or $\text{CHCl}=\text{CCl}_2$. Where recycle is practiced, the halohydrocarbons fed to the reaction zone typically include CHCl_2CF_3 in addition to CH_2ClCF_3 (starting material and/or recycle) and/or $\text{CHCl}=\text{CCl}_2$. Of particular note are embodiments where $\text{CHCl}=\text{CCl}_2$ starting material and CH_2ClCF_3 recycle (i.e., a saturated recycle) are reacted in a single reaction zone.

The molar ratio of chlorine to the total moles of $\text{CHCl}=\text{CCl}_2$, CH_2ClCF_3 and recycled CHCl_2CF_3 fed to the reaction zone is typically within the range from 0.5:1 to 50:1, and is preferably from 2:1 to 10:1.

The molar ratio of hydrogen fluoride to the total moles of $\text{CHCl}=\text{CCl}_2$, CH_2ClCF_3 and recycled CHCl_2CF_3 fed to the reaction zone is typically within the range of from 2:1 to 100:1, and is preferably from 3:1 to 30:1.

An inert diluent such as argon, helium, or nitrogen may be used in the chlorofluorination reaction of the present invention. If desired, oxygen may be cofed into the reaction zone. The molar ratio of oxygen which may be present during the reaction to the total moles of CH_2ClCF_3 , $\text{CHCl}=\text{CCl}_2$ and additional recycle, if any, can vary but will typically be within the range of from 0.001:1 to 1:1. The oxygen may be fed to the reaction zone as such or may be diluted with an inert gas such as

SUBSTITUTE SHEET

nitrogen, helium, or argon. The source of the oxygen may also be air.

The combination of components fed to the reaction zone (i.e., the CH_2ClCF_3 , $\text{CHCl}=\text{CCl}_2$, Cl_2 , HF and other components such as CHYClCF_3 , oxygen, and/or inert diluents) may be added individually or as mixtures of two or more of the components.

The reaction is conducted at elevated temperature. Generally, the reaction temperature can range from 200°C to 375°C, and is preferably from about 240°C to 310°C. The contact time generally will be from about 1 to 60 seconds, and is preferably from about 15 to 30 seconds. Although the chlorofluorination reaction of the present invention is usually conducted at atmospheric pressure, it may also be conducted under elevated or reduced pressure.

2-Chloro-1,1,1,2-tetrafluoroethane and pentafluoroethane in the gaseous mixture discharged from the reactor may be isolated by conventional means, such as distillation. Products of the chlorofluorination reaction of the formula CHYClCF_3 , where Y is selected from Cl and H, (i.e., CH_2ClCF_3 and/or CHCl_2CF_3) may be recycled to the chlorofluorination reaction zone to afford additional HCFC-124 and HFC-125.

HF may be present in some embodiment of the invention as an azeotrope or a mixture of azeotropes. Azeotropic compositions containing HF and CHYClCF_3 may also be recycled to the reactor.

Practice of the invention will become further apparent from the following non-limiting Examples.

EXAMPLE 1

Chlorofluorination of CH_2ClCF_3

A 15 in. (38.1 cm) x 3/8 in. (0.95 cm) Hastelloy™ nickel alloy tube was filled with 15.87 g of 12 to 20 mesh (1.7 to 0.84 mm) fresh chrome oxide. The catalyst

SUBSTITUTE SHEET

was activated by heating at 450°C for 1 hour under a nitrogen purge (50 sccm, 8.3×10^{-7} m³/s), then cooled to 300°C and purged with HF (20 sccm, 3.3×10^{-7} m³/s). The flow of HF was then raised to 140 sccm (2.3×10^{-6} m³/s) for one hour. The catalyst bed temperature was reduced to 269°C and CH₂ClCF₃, HF and Cl₂ were fed at 1.0 sccm (1.7×10^{-8} m³/s), 40.9 sccm (6.8×10^{-7} m³/s) and 18.4 sccm (3.1×10^{-7} m³/s), respectively. The results of this reaction are shown in Table 1. The bed temperature was then raised to 299°C and CH₂ClCF₃, HF and Cl₂ were fed at 0.52 sccm (8.7×10^{-9} m³/s), 58.1 sccm (9.7×10^{-7} m³/s) and 10.8 sccm (1.8×10^{-7} m³/s), respectively. The results of this second reaction are also shown in Table 1.

The reactor effluent was sampled on-line with a Hewlett Packard HP 5880 gas chromatograph using a 20 foot long, 1/8 inch diameter, column containing Krytox™ perfluorinated polyether on an inert support and a helium flow of 35 cc/minute. Gas chromatographic conditions were 70°C for 3 minutes followed by temperature programming to 180°C at a rate of 6°C/minute.

TABLE 1

| T (°C) | %124(a) | %125(b) | %123(c) | %114a(d) | %113(c) | %133a(f) | %114(g) | %115(h) |
|--------|---------|---------|---------|----------|---------|----------|---------|---------|
| 269 | 68 | 9.3 | 7.5 | 5.5 | 3.7 | 3.4 | 2.3 | - |
| 299 | - | 82 | 0.4 | 3.2 | - | 4.1 | 5.1 | 5.0 |

(a)124 = CHClFCF₃

(b)125 = CHF₂CF₃

(c)123 = CHCl₂CF₃

(d)114a = CCl₂FCF₃

(e)113 = CCl₂FCClF₂

(f)133a = CH₂ClCF₃

(g)114 = CCIF₂CClF₂

(h)115 = CCIF₂CF₃

SUBSTITUTE SHEET

HCFC-123 and HCFC-133a, after removal from the product mixture by distillation, may be recycled to the reaction zone to afford additional HCFC-124 and HFC-125.

EXAMPLE 2

5 Chlorofluorination of $\text{CHCl}=\text{CCl}_2$

A chrome oxide catalyst was prepared and used in the apparatus described in Example 1 except that 15.09 g of catalyst was used. The catalyst bed was cooled to 275°C and $\text{CHCl}=\text{CCl}_2$ (TCE), HF and Cl_2 were fed at
10 3.7 sccm ($6.2 \times 10^{-8} \text{ m}^3/\text{s}$), 2.3 sccm ($3.8 \times 10^{-8} \text{ m}^3/\text{s}$) and 28.9 sccm ($4.8 \times 10^{-7} \text{ m}^3/\text{s}$), respectively. The reactor effluent had a molar composition as shown in Table 2.

TABLE 2

| <u>%TCE</u> | <u>%124</u> | <u>%125</u> | <u>%123</u> | <u>%114a</u> | <u>%113</u> | <u>%133a</u> | <u>%114</u> | <u>%115</u> |
|-------------|-------------|-------------|-------------|--------------|-------------|--------------|-------------|-------------|
| 5.3 | 13.1 | 4.8 | 10.1 | 6.5 | 10.1 | 39.6 | 9.7 | 0.8 |

HCFC-123 and HCFC-133a, after removal from the product mixture by distillation, may be recycled to the
15 reaction zone to afford additional HCFC-124 and HFC-125.

Particular embodiments of the invention are illustrated by the examples. Other embodiments will become apparent to those skilled in the art from a consideration of the specification or practice of the
20 invention disclosed herein. It is understood that modifications and variations may be practiced without departing from the spirit and scope of the novel concepts of this invention. It is further understood that the invention is not confined to the particular
25 formulations and examples herein illustrated, but it embraces such modified forms thereof as come within the scope of the claims which follow.

SUBSTITUTE SHEET

WHAT IS CLAIMED IS:

1. A process for producing halohydrocarbon compounds of the formula CHXFCF_3 wherein X is selected
5 from the group consisting of Cl and F, characterized by:
 - (a) feeding a combination of components comprising (i) at least one halohydrocarbon starting compound selected from $\text{CHCl}=\text{CCl}_2$ and CH_2ClCF_3 , (ii) Cl_2 ,
10 (iii) HF and optionally, (iv) at least one halohydrocarbon recycle compound of the formula CHYClCF_3 where Y is selected from the group consisting of H and Cl to a reaction zone;
 - (b) contacting said combination of compounds in said reaction zone with a catalyst comprising
15 chromium oxide at an elevated temperature to produce reaction zone products containing halohydrocarbon reaction products of the formula CHXFCF_3 together with halohydrocarbons of the formula CHYClCF_3 ;
 - (c) recovering at least a portion of the
20 reaction products from the reaction zone including at least one halohydrocarbon of the formula CHXFCF_3 ;
 - (d) optionally recycling a portion of the reaction zone products to said reaction zone; and
 - (e) providing a catalyst contact time and
25 temperature in said reaction zone and an amount of recycle of halohydrocarbons of the formula CHYClCF_3 to said reaction zone sufficient to produce halohydrocarbon compounds of the formula CHXFCF_3 in said recovered reaction products as the major component of the halogen-
30 substituted hydrocarbon reaction products in said recovered reaction products.
2. The process of Claim 1 wherein the reaction temperature is within the range of from 200°C to 375°C ; wherein the molar ratio of Cl_2 to the total moles of
35 $\text{CHCl}=\text{CCl}_2$, CH_2ClCF_3 , and recycled CHCl_2CF_3 is within the

SUBSTITUTE SHEET

range of from 0.5:1 to 50:1; and wherein the molar ratio of HF to the total moles of $\text{CHCl}=\text{CCl}_2$, CH_2ClCF_3 , and recycled CHCl_2CF_3 is within the range of from 2:1 to 100:1.

5 3. The process of Claim 2 wherein the catalyst consists essentially of chromium oxide.

 4. The process of Claim 2 wherein the catalyst comprises Cr_2O_3 prepared by the pyrolysis of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and having an alkali metal content of about 100 ppm or
10 less.

 5. The process of Claim 2 wherein the halohydrocarbon starting compound is CH_2ClCF_3 .

 6. The process of any one of Claims 2 through 5 wherein CHClFCF_3 is the major component of the halogen-
15 substituted hydrocarbon reaction products recovered.

 7. The process of any one of Claims 2 through 5 wherein CHF_2CF_3 is the major component of the halogen-substituted reaction products recovered.

 8. The process of Claim 2 wherein the
20 halohydrocarbon starting compound is $\text{CHCl}=\text{CCl}_2$.

 9. The process of any one of claims 2, 3, 4, 5, and 8 wherein the process is run with recycle of at least one of said halohydrocarbons of the formula CHYClCF_3 .

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 93/10139

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C07C17/00 C07C17/20 C07C17/10 C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | WO,A,90 08755 (E.I. DU PONT DE NEMOURS AND COMPANY) 9 August 1990 see claims | 1 |
| A | EP,A,0 313 061 (E.I. DU PONT DE NEMOURS AND COMPANY) 26 April 1989 see page - | 1 |
| A | EP,A,0 456 552 (ATOCHEM) 13 November 1991 see the whole document | 1 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

28 January 1994

Date of mailing of the international search report

- 9. 02. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Bonneville, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US 93/10139

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| WO-A-9008755 | 09-08-90 | AU-B- 622295 | 02-04-92 |
| | | AU-A- 5164990 | 24-08-90 |
| | | CA-A- 2009189 | 03-08-90 |
| | | EP-A- 0455748 | 13-11-91 |
| | | JP-T- 4503215 | 11-06-92 |
| | | US-A- 5185482 | 09-02-93 |
| ----- | | | |
| EP-A-0313061 | 26-04-89 | US-A- 4843181 | 27-06-89 |
| | | AU-A- 2411588 | 27-04-89 |
| | | JP-A- 1146832 | 08-06-89 |
| ----- | | | |
| EP-A-0456552 | 13-11-91 | FR-A- 2661906 | 15-11-91 |
| | | AU-B- 630807 | 05-11-92 |
| | | AU-A- 7605391 | 14-11-91 |
| | | JP-A- 4226927 | 17-08-92 |
| | | KR-B- 9310404 | 23-10-93 |
| | | | |
| ----- | | | |